

Carbon Storage and Sequestration as Mineral Carbonates

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Abstract: The U.S. Department of Energy has identified mineral sequestration as a promising CO₂ sequestration technology option, converting anthropogenic CO₂ and magnesium silicates into permanent carbonate minerals. Advantages of a mineral CO₂ mitigation scheme include (1) enormous deposits of ultramafic rock such as serpentine [Mg₃Si₂O₅(OH)₄] and olivine [(Mg,Fe)₂SiO₄], exist in nature, providing a large potential capacity for CO₂ sequestration, (2) resulting magnesite (MgCO₃) product is thermodynamically stable and environmentally benign, and (3) overall process is exothermic with potential to be implemented with acceptable economics. High carbonation efficiencies were attained at elevated temperatures and supercritical CO₂ pressures employing magnesium silicate ores. However, unlike olivine, serpentine required an additional high temperature pre-treatment step to drive off hydroxyl groups prior to carbonation. X-ray diffraction analysis (XRD) identified magnesite as the primary reaction product. Mechanistic aspects of mineral dissolution/magnesium carbonate precipitation were investigated with the aid of scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS) of polished cross sections of solid process grains. Alterations to both thermally pre-treated serpentine and natural olivine grains revealed outer surfaces to be noticeably depleted in magnesium in comparison to its inner core. Formation of silica rims on the reaction surfaces may slow further dissolution of magnesium from silicate grains

Key words: CO₂ sequestration, mineral carbonation, ultramafic rocks, serpentine, olivine, carbon storage and sequestration, scanning electron microscopy-energy-dispersive spectroscopy (SEM-EDS)

1. INTRODUCTION

Fossil fuels are projected to be a dominant energy resource for the world's energy needs in the 21st century. Availability of these indigenous fuels—namely coal, oil, and natural gas—are essential for providing clean, affordable energy along with domestic and international prosperity and security. Today more than 86 percent of the world's commercial energy needs are supplied by fossil fuels. Conversely, accumulation of greenhouse gases in the atmosphere, in particular CO₂, and its potential role in precipitating climate change is recognized as a driving force in developing technologies for carbon sequestration. Within the U.S., nearly one-third of all anthropogenic CO₂ emissions are generated by stationary sources estimated at 6 GtC/year¹. The developments of a balanced “carbon-management” strategy to include technologies related to CO₂ sequestration will help resolve the energy-carbon challenge and meet the rapidly growing global requirements for energy. Fossil fuels are positioned to supply the world's energy needs for centuries to come if (1) suitable, environmentally benign, long-term CO₂ sequestration technologies can be developed and (2) CO₂ sequestration costs can be reduced to a competitive level.

A portfolio of carbon sequestration technologies is being explored to capture and store securely CO₂ that would otherwise be emitted to the atmosphere. Several relatively low-cost options for decreasing anthropogenic CO₂ sources such as improved energy generation efficiency, and renewable energy sources are being considered for their potential to be implemented relatively instantaneously. Although these CO₂ mitigation strategies may provide economic viability, they are not generally viewed as long-term solutions due to their limited mitigation capacity^{2,3}. Oceanic sequestration and CO₂ storage in geological media are two possible large-scale, long-term options with potential to sequester substantial amounts of CO₂. Although oceanic sequestration provides the most significant and largest natural sink for CO₂, the effects of permanently disposing CO₂ are not well known particularly the ocean chemistry in close proximity to the disposal site, fate of the CO₂ plume, and how marine life will be negatively affected. Candidate land-based subterranean reservoirs such as depleted oil and gas fields and deep saline aquifers provide large storage capacities for CO₂. In addition to being an immediately available option, oil and gas reservoirs also have the advantage of known geology, providing an adequate seal to contain injected CO₂ for hundreds of years. Close proximity to most large CO₂ generation sources highlights this prime sequestration option.

Mineral Carbonation offers a promising means of sequestering CO₂ permanently in an immobile, environmentally benign form⁴⁻²³. Mineral carbonation, alternately referred to as *Mineral Sequestration*, is the conversion of CO₂ with naturally occurring minerals to form geologically stable carbonate minerals. Drawing on mineral carbonation to sequester large volumes of anthropogenic CO₂ has numerous advantages. Initially, this approach emulates the natural chemical transformations of CO₂, such as weathering of ultramafic rocks to form calcium or magnesium carbonates. Thus, mineral carbonation ensures permanent fixation rather than temporary storage of CO₂ avoiding costly monitoring protection and potential lethal seepage. Second, geologic studies by Goff indicate total accessible amounts of these deposits, especially serpentines, exist in sufficient quantities far in excess of that needed to sequester all CO₂ that could be emitted from global coal reserves^{4,5}. Although olivine (Mg₂SiO₄) deposits are not as prolific as serpentine, they do occur in sufficient magnitude to be considered a viable candidate for mineral sequestration. Finally, the silicate mineral carbonation reaction is strongly exothermic (e.g., the overall energy released during serpentine carbonation is 15 kcal/mol), providing clear energy and process cost advantages⁴. The transformation of serpentine, Mg₃Si₂O₅(OH)₄, and CO₂ into magnesite, MgCO₃, and silica is illustrated below. In this ideal case, one ton of serpentine can dispose of approximately one-half ton of CO₂. The reaction is exothermic and releases 64 KJ/mole (~2,300 Btu/lbC).



The focus of this chapter was to use these natural, magnesium based silicates as a feed stream within a continuous-stirred-tank-reactor (CSTR) for investigating experimental parameters in accelerating carbonation rates; examining thermal pretreatment methods to enhance serpentine reactivity; and analyzing structural changes to feed and process particles for identifying magnesium dissolution/magnesium carbonate precipitation reaction paths and potential barriers.

2. Experimental

2.1 Mineral Carbonation Experiments

Mineral carbonation experiments were carried out in a 1-liter Hastelloy C-2000 CSTR unit. In a representative experiment, 40.0 grams of pulverized magnesium based silicate (serpentine or olivine) particles with 360.0 g of bicarbonate aqueous solution (0.5M Na₂CO₃; 0.5M Na₂HCO₃; 1.0M NaCl or 0.5M NaHCO₃) was charged into the CSTR. The CSTR was sealed, and

purged with gaseous carbon dioxide. A pre-calculated amount of liquid CO₂ was then injected through the side port of the CSTR. The magnesium silicate ore/bicarbonate aqueous solution/liquid CO₂ mixture was sufficiently agitated during both heat up and testing to prevent any settling of magnesium silicate ore. At the conclusion of each test, the remaining CO₂ was vented, and the carbonated slurry was flushed from the CSTR and filtered to separate solids from the bicarbonate aqueous solution. The washed carbonated solid product was dried at 105°C in air overnight. A digital pH meter determined pH values of pre- and post-product solutions.

2.2 X-ray powder diffraction (XRD)

XRD measurements of untreated and CO₂-treated magnesium silicate ores were carried out using a Rigaku DAD-IIA powder diffractometer with a Cu-K α X-ray source at 40kV and 25 mA. The powder sample was mounted on a glass sample holder. The XRD patterns were recorded over a 2 θ range of 2° to 90° and compared with the JCPDS mineral powder diffraction file.

2.3 X-ray photoelectron spectroscopy (XPS)

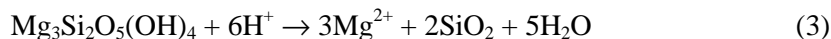
XPS analyses were carried out using a PHI 5600ci spectrometer. A standard Al K α (1486.6 eV) X-ray source was used at a power of 400 W, with the analysis chamber typically maintained at less than 5 X10⁻⁹ Torr. The pass energy of the analyzer was 58.7 eV. Binding energies were corrected for charging using the adventitious carbon peak at 284.6 eV. All magnesium silicate ores were analyzed after dusting onto double-sided conductive sticky tape.

2.4 Scanning Electron Microscopy (SEM)

SEM analyses were performed using an Aspex Personal SEM™ equipped with a Noran energy dispersive detector enabling x-ray detection of elements with atomic number 6 (carbon) and greater. Sample preparation involved mounting a portion of a representative sample in epoxy and polishing to get a cross section of the particles. Polished cross sections of serpentine, olivine and their respective solid products were analysed at an accelerating voltage of 20 KeV and working distance of 16-19 mm. Prior to analyses, samples were coated with a thin layer of carbon to provide an electrically conductive surface. The samples were examined in backscattered electron imaging (BSI) mode coupled with energy dispersive spectroscopy (EDS).

3. Results and Discussion

Possible reactions between mineral reactants, such as serpentine and CO₂ may be represented by a simple set of chemical reactions:



The dissolution of CO₂ in water forms carbonic acid, which proceeds to dissociate into hydrogen and bicarbonate ions (Equation 2). The reaction of carbonic acid with serpentine consumes most of the hydrogen ions, liberating Mg²⁺ cations, along with forming free silica and water (Equation 3).

Mineral precipitation



Dissolved ionic species (Mg²⁺, HCO₃⁻) combine to form the solid carbonate mineral, magnesite (Equation 4). Although the above reaction proceeds spontaneously due to the negative Gibbs free energy change, the reaction rate is extremely slow under ambient temperature and pressure. Thus, laboratory parametric testing at higher temperatures and pressures was necessary to help accelerate carbonation rates.

A Cedar Hills serpentine (antigorite) sample obtained from the Pennsylvania/Maryland State line district was selected for mineral carbonation testing. Chemical analyses of serpentine feed, thermally pre-treated serpentine (200 & 650°C for 2 hrs.) prior to carbonation, and their corresponding product solids after carbonation are shown in Table 1. XRD identified antigorite as being the primary constituent in the raw, serpentine feed (Figure 1). Trace elements of chrysotile, forsterite, and magnetite were also present. A modest increase in magnesium oxide content (Table 1) for the “serpentine HT650 sample” (44 weight percent) in comparison to the original serpentine feed (42 weight percent) was attributed to the removal of hydroxyl groups from the serpentine ore upon heating. Thermal pre-treatment of the serpentine feed was found necessary to improve rate of magnesite conversion.

XRD analysis (Figure 2) showed forsterite being the primary constituent in the “serpentine HT650 sample” prior to carbonation testing. Transformation of serpentine, a Mg-rich lamellar hydroxide based mineral, to forsterite was attributed to the disordering around the magnesium local

structure, making it more reactive or facilitating dissolution into the aqueous phase. XRD analysis (Figure 3) coupled with a high CO₂ concentration in the reaction products (Table 1), confirmed MgCO₃ as the major element for the serpentine HT650 reaction product.

Table 1.
Chemical Analysis of Serpentine Feed
Thermally pre-treated Serpentine, and Reaction Products (wt. percent)

Oxide	Cedar Hills Serpentine ¹	Cedar Hills Serpentine HT650 ²	Cedar Hills Serpentine HT200 ³	Serpentine HT650 Carbonated Product ⁴	Serpentine HT200 Carbonated Product ⁵
Al ₂ O ₃	0.21	1.21	0.29	1.46	0.24
CaO	0.14	0.39	0.13	0.25	1.03
Fe ₂ O ₃	4.66	7.81	4.49	5.42	4.58
K ₂ O	0.02	0.02	0.01	0.01	0.01
MgO	41.82	43.59	40.62	30.29	41.25
NaO	0.02	0.04	0.48	0.79	0.01
SiO ₂	38.74	44.97	37.61	31.13	38.08
TiO ₂	0.01	0.01	0.01	0.01	0.01
P ₂ O ₅	0.01	0.01	0.01	0.01	0.01
Volatiles ⁶	14.2	2.5	13.2	30.1	15.4
Total	99.8	100.5	97.0	99.6	99.8

¹Serpentine, Cedar Hills, “as received” feed sample. ²Serpentine, Cedar Hills, heat-treated in air at 650°C for 2 hours. ³Serpentine, Cedar Hills, heat-treated in air at 200°C for 2 hours.

⁴Carbonated solid product of Serpentine, Cedar Hills, heat-treated in air at 650°C for 2 hours.

⁵Carbonated solid product of Serpentine, Cedar Hills, heat-treated in air at 200°C for 2 hours.

⁶Volatile constituents include: mineral carbon, fixed carbon, and moisture

Results obtained from experiments investigating the reactivity of serpentine (Cedar Hills, USA) and olivine (Twin Sisters Range, USA) in aqueous, bicarbonate aqueous, and carbonate/bicarbonate solutions are shown in Table 2. Initial serpentine carbonation tests in distilled water resulted in much lower conversions compared to identical tests conducted with the natural silicate mineral, olivine. Subsequent testing (in distilled water) showed marginal improvement in conversion using a thermally pre-treated serpentine (pre-treated in air @ 650°C prior to carbonation) sample. Significant improvement in mineral carbonation efficiency was further established by additions of NaHCO₃ and NaCl to the aqueous solution. The interaction of thermally pre-heated serpentine samples with supercritical CO₂ in buffered solutions (0.5M NaHCO₃, 1M NaCl or 0.5 M Na₂CO₃ / 0.5 M NaHCO₃; 1 M NaCl) were found to induce significant increases in both rate

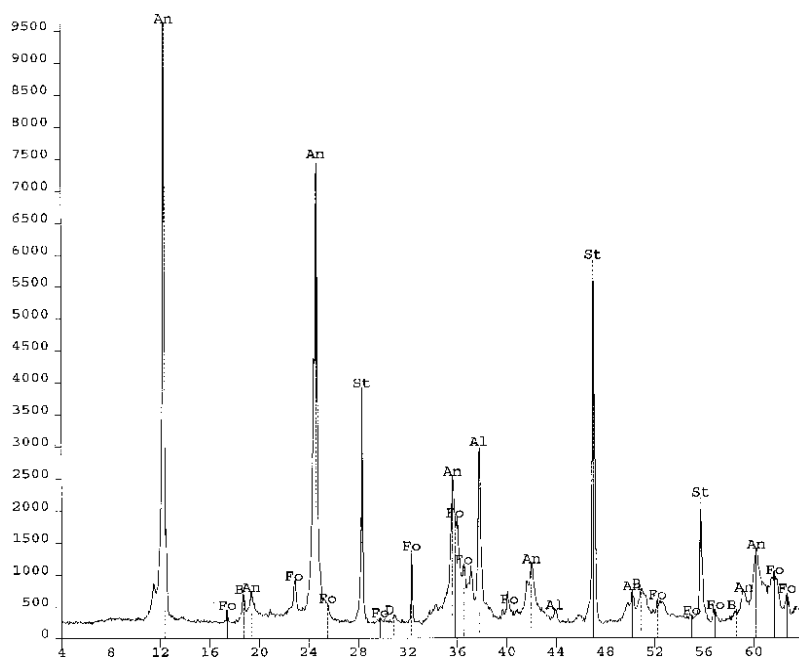
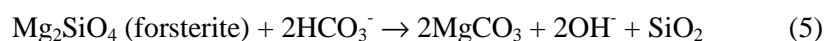


Figure 1. X-ray diffraction pattern for Cedar Hills serpentine (antigorite) feed sample. Pattern scheme: antigorite (An), forsterite (Fo), calcium fluoride (St)

and conversion, although the reactions still required several hours to achieve significant carbonation. The increased rate was attributed to the increased solubility of carbon dioxide in the aqueous phase. In substituting a 0.5M NaHCO_3 , 1M NaCl buffered solution for distilled water, the extent of reaction increased to 83% for the serpentine sample thermally pre-treated in CO_2 as compared to 84% for the untreated, natural olivine. These results clearly illustrated the bicarbonate ions in solution react readily with Mg_2SiO_4 (forsterite), producing the desired carbonate product, magnesite, with hydroxide ions, and free silica (Equation 5).



The resulting hydroxide ions immediately reacted with the absorbed CO_2 in the liquid phase to re-establish the high bicarbonate concentration (Equation 6).



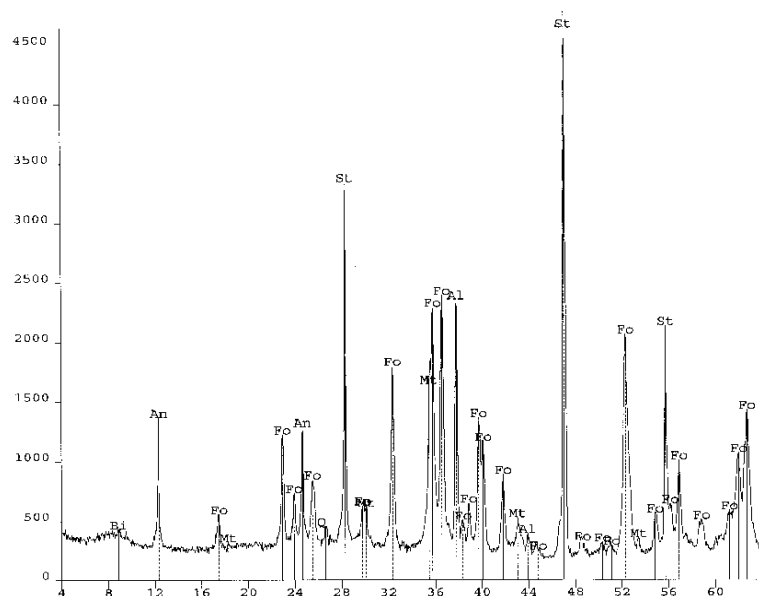


Figure 2. X-ray diffraction pattern of Cedar Hills serpentine HT650 sample. Pattern scheme: antigorite (An), forsterite (Fo), calcium fluoride (St)

The *in-situ* pH of the aqueous slurry /liquid CO₂ system could not be accurately determined however, pre- and post-test pH values of the carbonated solution remained relatively constant.

XPS was employed to study the surface alteration of both serpentine and olivine feed samples before and after the interaction of CO₂ at reaction temperatures and pressures. The relative atomic abundance of cations (Mg, Si) for the untreated minerals were consistent with the formal compositions of serpentine (3:2) and olivine (2:1). Representative XPS C 1s spectra for the olivine (Twin Sisters Range, USA) sample is presented in Figure 4. Analyses of the solid reaction product obtained after mineral carbonation testing showed clear confirmation from the C 1s peak at 289.9 eV that CO₃ was present. The atomic ratios of Mg and C as carbonate were almost 1:1, indicating that all of the Mg in the near surface reacted. The abundance of Mg, relative to silica, in both the near olivine and serpentine surfaces significantly decreased upon mineral carbonation processing. Thermal pre-

treatment of serpentine at 650°C prior to serpentine carbonation testing also led to surface depletion of magnesium in the reactant sample.

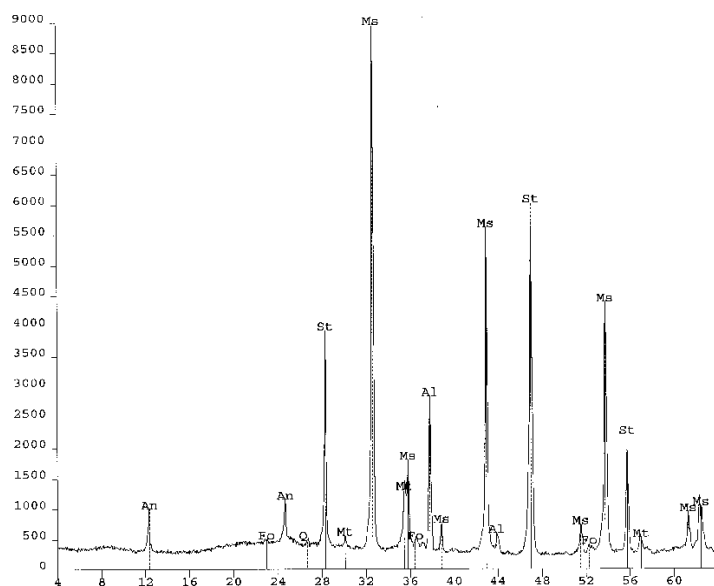


Figure 3. X-ray diffraction pattern of Cedar Hills serpentine HT650 reaction product. Pattern scheme: magnesite (Ms), antigorite (An), forsterite (Fo), calcium fluoride (St).

The O 1s binding energy (531.4 eV) was higher for the leached phase relative to the unleached phase, and comparable to what has been reported for other carbonates. The overall O 1s peak envelope probably reflects contributions from more than one oxygen-containing phase, including the carbonate and possibly silicon dioxide (quartz and silica gel) if $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ were also formed on the reaction product surface.

Polished cross sections of both thermally pre-heated serpentine and olivine process products were prepared for investigation using scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS) [Figures 5-12]. Results from these studies were envisioned to provide insight regarding carbonate precipitation along with magnesium, and silica occurrence within process products (along with possible intermediate products). Comprehension of magnesium, iron, and silica dissolution and precipitation characteristics provided insight into developing a fundamental understanding of the mechanistic aspects of the carbonation process.

Table 2. Summary of Cedar Hills Serpentine Carbonation Experiments

Reactant	Carbonation solution	% Conversion
Olivine ¹	Distilled H ₂ O	91
Serpentine ²	Distilled H ₂ O	34
Serpentine ³	Distilled H ₂ O	57
Serpentine ⁴	0.5 M NaHCO ₃ ; 1 M NaCl	83
Olivine ⁵	0.5 M NaHCO ₃ ; 1 M NaCl	84
Serpentine ⁶	0.5 M NaHCO ₃ ; 1 M NaCl	79
Olivine ⁷	0.5 M Na ₂ CO ₃ / 0.5 M NaHCO ₃ ; 1 M NaCl	85
Olivine ⁸	0.5 M Na ₂ CO ₃ / 0.5 M NaHCO ₃ ; 1 M NaCl	75
Serpentine ⁹	0.5 M Na ₂ CO ₃ / 0.5 M NaHCO ₃ ; 1 M NaCl	79

¹Olivine, Twin Sisters Range, USA; P=115 atm.; T=185°C; Time = 24 hrs.

²Serpentine, Cedar Hills, USA; P=115 atm.; T=185°C; Time = 24 hrs.

³Serpentine; heat-treated in air at 650°C; P=115 atm.; T=185°C; Time = 24 hrs.

⁴Serpentine; heat-treated in CO₂ at 650°C; P=115 atm.; T=185°C; Time = 6 hrs.

⁵Olivine, Twin Sisters Range, USA; P=115 atm.; T=185°C; Time = 6 hrs.

⁶Serpentine; heat-treated in air at 650°C; P=115 atm.; T=185°C; Time = 3 hrs.

⁷Olivine, Twin Sisters Range, USA; P=115 atm.; T=155°C; Time = 3 hrs.

⁸Olivine, Twin Sisters Range, USA; P=115 atm.; T=185°C; Time = 3 hrs.

⁹Serpentine; heat-treated in air at 650°C; P=115 atm.; T=185°C; Time = 3 hrs.

Particle size for all Serpentine and Olivine experiments was ~75 microns.

In Figures 5 and 7, SEM with EDS spectra focused on the interior core of a number of large, cross sectional portions (>10µm) of the serpentine HT650 reaction product. The cross sectional portion of these grains appeared to be nonporous, free of cracks and fractures, having undergone little or no alteration at all. Indeed, the SEM with EDS spectra of the serpentine HT650 interior core showed very uniform concentrations of both magnesium and silica. These results clearly demonstrated magnesium dissolution to be negligible at the core of the grain. Iron oxide, in the form of magnetite, also remained relatively inert inside the serpentine HT650 grain.

Figures 6 and 8 show a series of SEM photomicrographs with EDS spectra obtained for the serpentine HT 650 reaction product. SEM with EDS spectra identified the majority of the fine particles (10µm and less) within the representative sample to contain high concentrations of magnesium and oxygen with trace amounts of silica (Figure 6). Such a result is consistent with ICP-AES analysis, which determined an 80% stoichiometric conversion for the serpentine HT650 substrate to carbonate (Table 2). These results are clearly indicative of precipitation being the predominate mechanism in forming the reaction product, magnesite. SEM-EDS analysis also showed small, representative particles (<10µm) containing high concentrations of silica (Figure 8). These dispersed particles appear to represent the primary

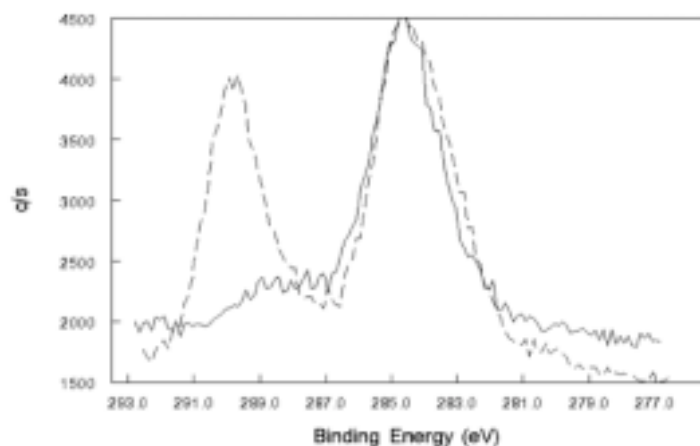


Figure 4. Typical C 1s spectra of natural olivine after mineral carbonation process. Solid and dashed lines indicate starting and reaction product phases respectively.

fate of silica, in forming stacks of amorphous silica. In summary, the free silica did not appear to agglomerate with or precipitate onto the magnesite particles to any appreciable degree. Such a result is viewed as favourable for developing post-treatment schemes dedicated to by-product recovery.

Figures 9,10, and 11 illustrates the information obtained on examining both the interior core and exterior edges of a single, cross sectional portion ($>10\mu\text{m}$) of the natural olivine reaction product. Analogous to the serpentine HT650 product described in Figure 5, this grain also appears to be nonporous, free of cracks and fractures, having undergone little or no alteration. The SEM with EDS spectra of the natural olivine's interior core shows very uniform concentrations both in magnesium and silica (Figure 11). However, analysis by SEM-EDS on the grain's perimeter clearly shows a definite alteration rim, providing evidence for an altered olivine-magnesite particle. The EDS spectra clearly showed this observable reaction rim to be extremely depleted in Mg, as depicted in Figure 9, in comparison to its interior core, as illustrated in Figure 11. This evidence was further supported by SEM-EDS analysis on the identical grain's exterior edges showing high concentrations of magnesium and oxygen but void of silica (Figure 10). Possible armoring of the silicate particles by silica and/or magnesium carbonate precipitation could have the potential of hindering further dissolution of magnesium, establishing reaction as diffusion limited.

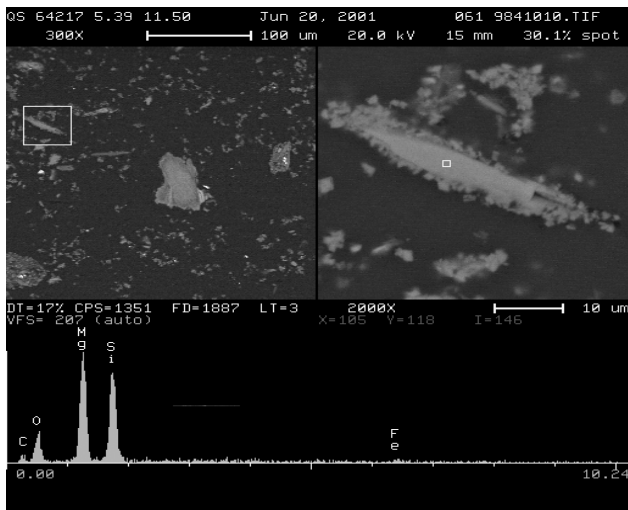


Figure 5. Serpentine HT 650 reaction product, Cedar Hills, USA. SEM-EDS analysis showing interior of particle containing high concentrations of magnesium and silica. Reaction product grain represents one having undergone little or no alteration.

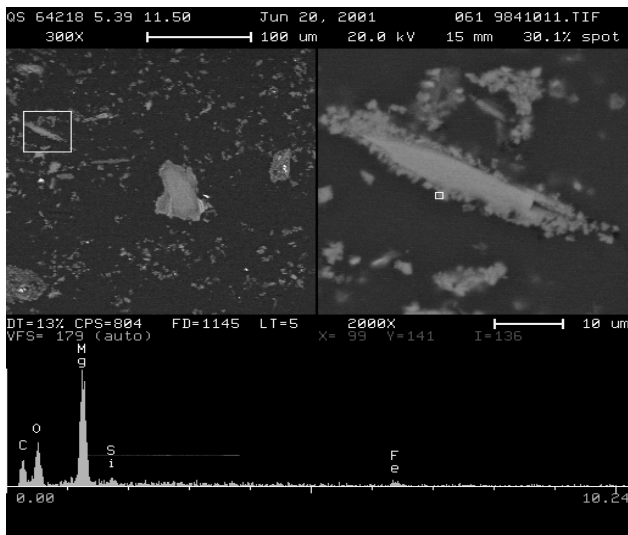


Figure 6. Serpentine HT650 reaction product, Cedar Hills, USA. SEM-EDS analysis showing outside edge of particle containing high concentrations of magnesium with a trace concentration of silica. Reaction product represents precipitated magnesite particles surrounding an altered serpentine grain.

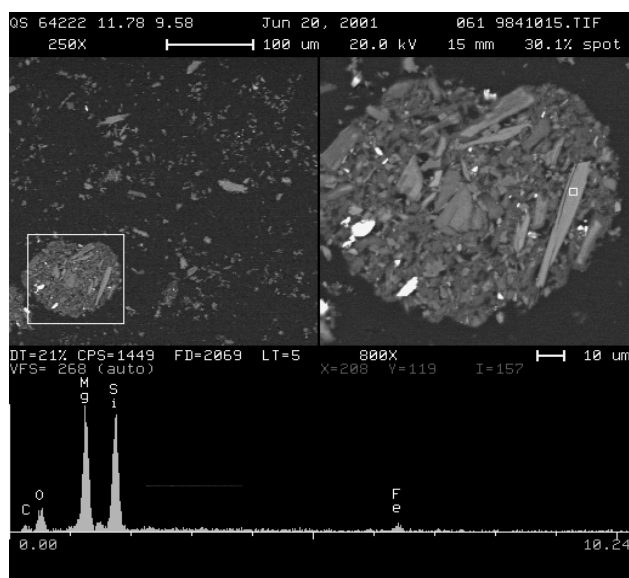


Figure 7. Serpentine HT 650 reaction product, Cedar Hills, USA. SEM-EDS analysis showing long, fibrous particle containing high concentrations of magnesium and silica. Reaction product grain represents one having undergone little or no alteration.

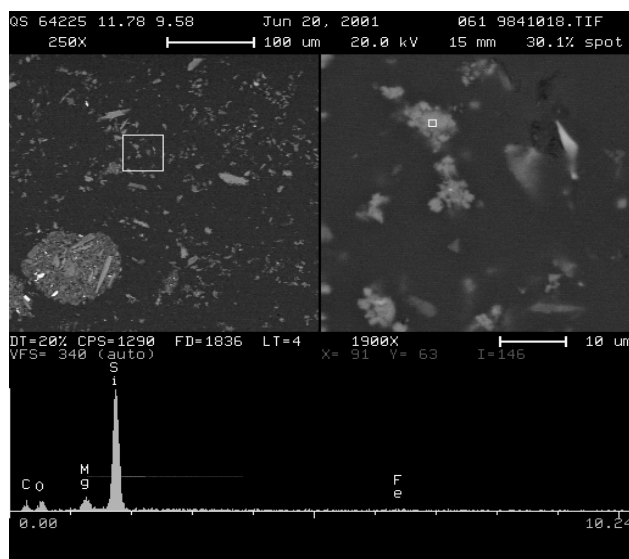


Figure 8. Serpentine HT 650 reaction product, Cedar Hills, USA. SEM-EDS analysis showing large grains containing high concentrations of silica with trace amount of magnesium. Reaction product would appear to represent a separate silica grain.

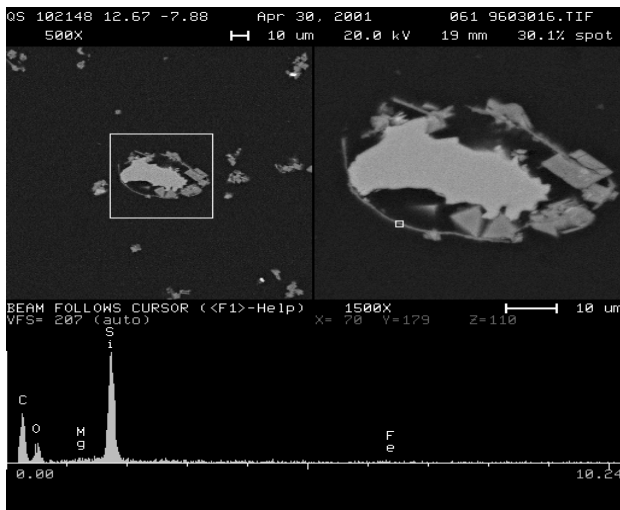


Figure 9. Olivine, Twins Sisters Range, USA. SEM-EDS analysis showing outer edge of particle containing high concentration of silica. . Reaction product represents an altered olivine particle significantly depleted in magnesium.

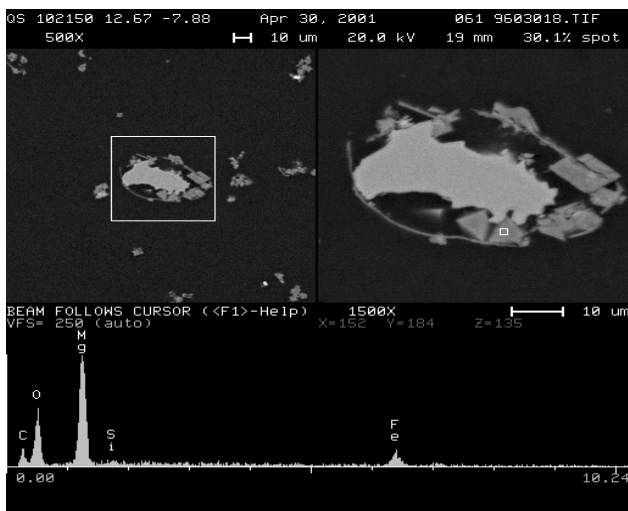


Figure 10. Olivine, Twin Sisters Range, USA. SEM-EDS analysis showing triangular and rhombohedral grains containing high concentrations of magnesium and oxygen. . Reaction product represents a precipitated magnesite grain in close proximity to a significantly altered olivine particle.

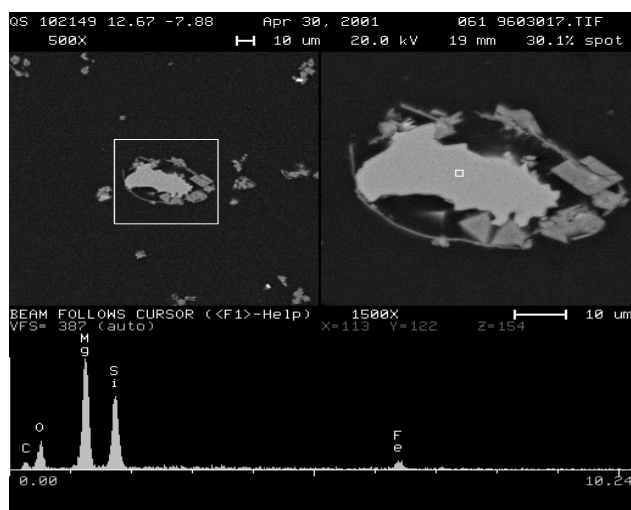


Figure 11. Olivine, Twin Sisters Range, USA. SEM-EDX analysis showing interior of large particle containing high concentrations of magnesium and silica. Reaction product grain represents one having undergone little or no alteration. (Unaltered olivine core)

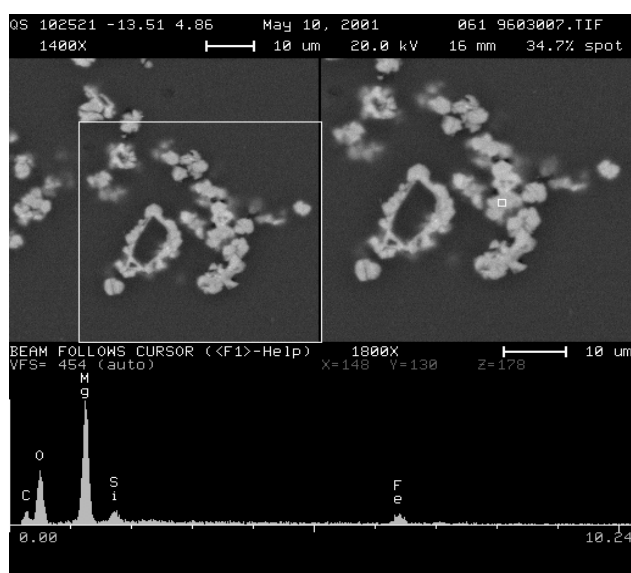


Figure 12. Olivine, Twin Sisters Range, USA. SEM-EDX analysis showing round particles containing high concentrations of magnesium, carbon, and oxygen. Reaction product represents a cluster of separate magnesium carbonate grains.

4. CONCLUSIONS

The U.S. Department of Energy has identified mineral sequestration as a long-term, environmentally benign, and unmonitored option for storing CO₂. Experimental investigations confirm ultramafic minerals; serpentine and olivine are equally amenable to the mineral carbonation process, although serpentine requires an additional thermal pre-treatment step. Thermal pre-treatment of serpentine at 650°C removes hydroxyl groups resulting in the chemical transformation to forsterite with dramatically enhanced carbonation reactivity. High carbonation efficiencies were achieved under 3 hours in CSTRs utilizing a thermally pre-treated, pulverized serpentine reacted at temperatures of 155-185°C in high pressure CO₂ solutions, containing NaCl and sodium bicarbonate, NaHCO₃. Magnesite was identified as primary reaction product in the mineral carbonation process. XPS and SEM-EDS provided valuable information about both the elemental composition and bonding states of the starting reactant minerals and reaction products. Fundamental insights into the mineral dissolution and carbonate precipitation reaction pathways were investigated. Key findings include (i) Mineral carbonation requires mineral dissolution into aqueous phase, (ii) precipitation is primary mechanism in forming reaction product, magnesite, (iii) formation of silica enriched zones depleted of magnesium suggests the reaction could be diffusion resistant.

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